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## Shallow Acceptors in Cadmium Telluride

By

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The photoluminescence spectroscopy of undoped CdTe crystals provides information on two acceptors which are the main contaminants of as-grown crystals. These acceptors called  $y$  and  $z$  have their respective ionization energies at 147 and 108 meV. A complete series of two hole replicas is observed for  $y$  and only one for  $z$ . These acceptors are believed to be due to Cu and Ag impurities. Backdoping experiments with Li and Na give rise to new transitions. From the conduction band-acceptor level transitions, the ionization energies are respectively obtained to 57.8 and 58.8 meV. In the case of Li, some extra-lines are tentatively identified as phonon interacting two-hole transitions.

La spectroscopie de la photoluminescence de CdTe non dopé fournit des informations sur deux accepteurs qui sont des contaminants du matériau brut de croissance. Ces accepteurs, appelés  $y$  et  $z$  ont leurs énergies d'ionisation respectivement à 147 et 108 meV. Une série complète de répliques à deux trous a été observée pour  $y$  et seulement une réplique pour  $z$ . Ces accepteurs sont probablement dus aux impuretés Cu et Ag. Des expériences de dopage avec Li et Na donnent naissance à de nouvelles transitions. A partir des recombinaisons bande de conduction-niveau accepteur, les énergies d'ionisation ont été respectivement obtenues à 57,8 et 58,8 meV. Dans le cas du Li, des raies supplémentaires sont attribuées à une transition à deux trous, perturbée par une interaction avec des phonons.

### 1. Introduction

CdTe is the only II-VI semiconductor which can be obtained with conductivity of n- or p-type. Numerous studies have been made on CdTe [1], but there are only few precise results on shallow acceptors and donors, because most of works have been devoted to deep centers and high resistivity self-compensated materials. In fact, the observed levels have been frequently attributed to native defects (Cd vacancy or interstitial) and defect impurity complexes (Cd vacancy-donor) [2]. This approach may be largely incorrect, since it is now recognized from recent works on other II-VI compounds (e.g. ZnTe) that shallow impurity centers play a dominant role in the conductivity control of II-VI materials [3 to 6]. So it seems of first importance to clarify the respective roles of impurities and native defects in CdTe.

We report on the luminescence properties of four acceptors in CdTe. In high purity p-type material, two unidentified acceptors are observed. After backdoping experiments, we show that Li and Na introduce two other shallow acceptor levels. For the first time, we have observed "two-hole" transitions<sup>2)</sup> in this material.

### 2. Experimental

CdTe samples were sliced from ingots ( $\varnothing$  45 mm) obtained by a Bridgman method in excess tellurium (B. Schaub LETI Grenoble). Each slice contains a few monocrystalline grains, and is mechanically and chemically polished (in Br-methanol

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<sup>2)</sup> For a review of bound exciton problems see [7].

solution 2%). Crystals are not intentionally doped, and they are high purity p-type ( $N_A - N_D \approx 5 \times 10^{14} \text{ cm}^{-3}$ ).

Anneals are made in a quartz tube at 700 to 800 °C, under Te atmosphere and for durations ranging between few minutes and several days. Quenching is performed by immersing the tube in cold water.

Li and Na diffusions are made from nitrate solutions deposited on a polished surface, and in a horizontal furnace, under a continuous flow of  $\text{H}_2\text{-N}_2$  mixture. Temperatures are between 300 and 500 °C, and the typical annealing time is one hour. Annealing of the as-grown samples is performed with a similar experimental set-up, but without impurity sources and in non-contaminated tubes.

Before electrical and optical measurements, rectangular ( $10 \times 3 \text{ mm}^2$ ) samples are bevelled and etched, in order to explore the whole thickness of the sample.

Electrical measurements (capacitance/voltage) made on Schottky diodes, give the uncompensated acceptor concentration. The Schottky electrode is obtained by vacuum evaporation of indium through a metallic mask. The ohmic contact is provided by an electroless gold deposit on the back side of the sample.

Photoluminescence (PL) experiments are performed at 5 K. Samples are mounted in stress-free conditions in a variable temperature cryostat. The 4880 or 5145 Å lines of an  $\text{Ar}^+$  laser are used as excitation source, operating at a power of about 50 mW. The laser beam is modulated by a mechanical chopper, and the luminescence is focused on the entrance slit of a 3/4 m grating monochromator. A resolution better than 0.5 Å can be obtained. The signal is detected by cooled GaAs or Si cathode of a photomultiplier, and is analysed by a lock-in amplifier.

The light of a spectral lamp can be superposed (after being modulated by the chopper) on the luminescence beam, in order to calibrate the apparatus. So, the luminescence lines of different spectra can be compared easily with a great precision (better than 0.5 Å), and eventual stress (due to uncorrect sample mounting) inducing variations or shifts in the spectra can be detected.

### 3. As-Grown and Annealed CdTe

The PL spectra of the high purity p-type CdTe are dominated by a sharp line  $A_1^y$  at 1.5896 eV (Fig. 1) (we use the relation  $E(\text{eV}) \cdot \lambda(\text{Å}) = 12395.13$  for the wavelength-energy conversion [8]). A weaker line  $A_1^z$  at 1.5886 eV is also present. These sharp lines ( $\Delta E < 0.2 \text{ meV} < kT$ ) are the principal bound exciton (PBE) lines of the unknown acceptors “y” and “z”. At low temperatures, the photocreated electron-hole pairs interact strongly with acceptor or donor centers in the crystal, and form bound excitons [7, 9]. In our p-type crystals, we are concerned by neutral acceptor-bound exciton complexes, which involve three particles: two holes and one electron.

After the annihilation of the exciton, if the hole of the neutral acceptor is left in its ground state, we observe the PBE line  $A_1^x$  (x: acceptor name) at the energy

$$h\nu = E_G - E_{FE} - E_{LOC} \quad (1)$$

with  $E_G$  the band gap energy,  $E_{FE}$  the free exciton binding energy, and  $E_{LOC}$  the localization energy of the bound exciton.

In some of the recombination events, the hole of the neutral acceptor can be left in an excited state. After a theoretical model which takes into account the valence band degeneracy [10], the hole states can be classified in S- and P-like states. Then if the hole is left in its  $n$ -th (S or P) excited state with the binding energy  $E_n$ , we observe a luminescence line  $A_n^x$  shifted by  $E_1 - E_n$  from the PBE line.  $E_1$  is the ground state energy (i.e.  $E_A$ , the acceptor binding energy). These  $A_n^x$  lines are the so-called “two-hole transitions” (THT) (similarly, for donors, there are two-electron transitions

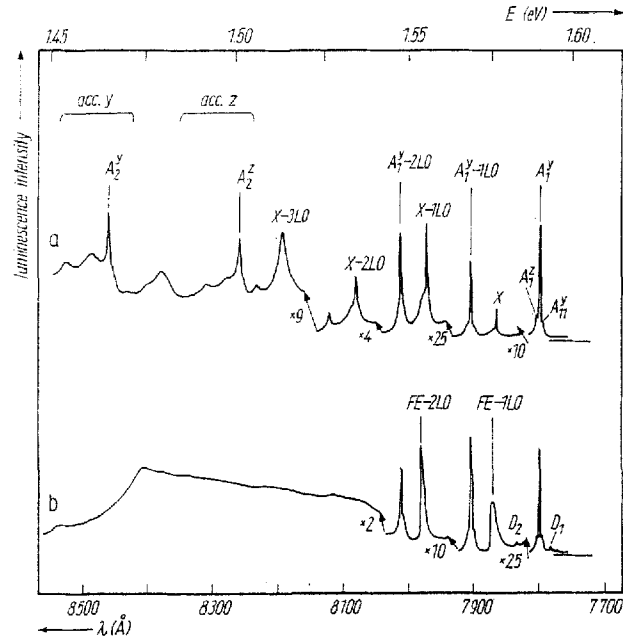


Fig. 1. Photoluminescence spectra of undoped p-type CdTe, recorded at 5 K (a) after annealing at 700 °C for 30 min under Te atmosphere ( $N_A - N_D \approx 2 \times 10^{15} \text{ cm}^{-3}$ ), (b) as-grown ( $N_A - N_D \approx 5 \times 10^{14} \text{ cm}^{-3}$ )

(TET). Due to the parity selection rules, in luminescence one can observe essentially transitions to S-like states [7].

Fig. 1 (curve a) shows THT for acceptors “y” and “z”.  $A_2^y$  and  $A_2^z$  are, respectively, shifted from  $A_1^y$  and  $A_1^z$  by 124.4 and 87.6 meV, while, in contrast, the PBE lines are shifted by only  $\approx 1$  meV. This is due to the fact that the exciton binding on a neutral acceptor is dominated by interparticle correlations but not by the central cell potential of the acceptor. On the other hand, the shift of the THT from the PBE line, depends directly on the acceptor binding energy, and therefore on the central cell corrections.

Fig. 1, curve a is obtained on a sample annealed under Te atmosphere at 700 °C for 30 min.  $N_A - N_D$  is about  $2 \times 10^{15} \text{ cm}^{-3}$ . For comparison, we show the PL spectrum of an as-grown sample (Fig. 1, curve b), which shows only the PBE lines, but not the THT lines. The band near 8400 Å is still unidentified but it disappears after any heat treatment. In the as-grown sample ( $N_A - N_D \approx 5 \times 10^{14} \text{ cm}^{-3}$ ) we can also see the donor related lines, but they are weaker than the acceptor lines.  $D_1$  is the PBE line of the donor, while in the  $D_2$  series, there are TET lines. The shift between  $D_1$  and  $D_2$  is the difference  $E_{1s} - E_{2s}$  of the donor. We find 10.3 meV, which gives  $E_D = 13.7$  meV for the binding energy of this unidentified donor. Assuming this is the effective mass binding energy, taking  $m_e = 0.0963m_0$  [11] for the electron effective mass, we get  $\varepsilon = 9.8$  for the dielectric constant.

On the spectra, we observe also a series of LO phonon replicas (in CdTe the LO phonon energy is 21.3 meV). Their intensities are well fitted by a Poisson distribution [12],

$$I_n = I_0 \bar{N}^n / n! , \quad (2)$$

where  $I_n$  is  $n$ -th replica intensity, and  $\bar{N}$  is the coupling constant, which reflects the strength of the electron-phonon coupling. For shallow acceptors, we find a weak coupling constant  $\bar{N} \approx 0.06$  as can be expected.<sup>3)</sup>

The line labeled X at 1.5762 eV (Fig. 1a) is just superimposed on the high energy side of the free exciton LO replica. This line is more strongly lattice coupled ( $\bar{N} \approx 0.15$ ). Its origin is still unknown but similar lines have already been observed in other II-VI materials, as in ZnSe ( $I_1$  deep) [13] or in ZnTe (X) [14].

### 3.1 Acceptor y

Fig. 2 shows the evolution of the PL spectra, for several annealing times, at 700 °C under Te atmosphere. When this time increases, the spectra are progressively dominated by only the acceptor "y" related lines. They can be separated in two parts. First the excitonic region near the band-gap edge (i.e. PBE line) and secondly the low energy side concerning THT lines and/or large bands resulting from transitions between donors and acceptors (DAP) or between conduction band and acceptors.

After short anneals,  $N_A - N_D$  is between  $10^{16} \text{ cm}^{-3}$  at the surface, and a few  $10^{15} \text{ cm}^{-3}$  in the bulk of the samples. In Fig. 2, curve a, which is an enlarged view of Fig. 1, curve a, the spectrum recorded after a 30 min anneal, we can only see the THT lines  $A_n^y$  and the PBE lines  $A_1^y$  as well as  $A_1^z$  (the acceptor z is still important after such a short anneal). After 6 h anneal, near the surface of the sample,  $A_1^y$  dominates the spectrum, but it is broader (Fig. 2, curve b). Near 8500 Å, we observe the emergence of the DAP band ( $D^0, A_y^0$ ), at the expense of the THT lines. Only  $A_2^y$  can still be seen.

After a longer anneal (6 days)  $N_A - N_D$  becomes  $9 \times 10^{16} \text{ cm}^{-3}$  throughout the sample (Fig. 2, curve c).  $A_1^y$  is replaced by a broad band, with some "undulations" on the low energy tail. This phenomenon is well known, and has been observed in GaP [15] and also for all the acceptors in ZnTe [16, 17].

In fact, when the acceptor concentration increases, the mean distance between acceptor sites decreases, and so bound excitons are delocalized on several interacting

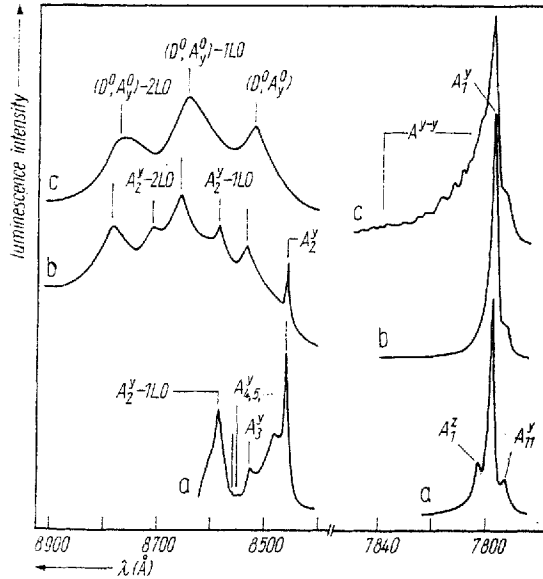


Fig. 2. Photoluminescence of CdTe at 5 K, for different acceptor concentrations: (a)  $N_A - N_D = 2 \times 10^{15}$ , (b)  $10^{16}$ , (c)  $9 \times 10^{16} \text{ cm}^{-3}$ . ( $D^0, A_y^0$ ) is donor-acceptor pair band.  $A_n^y$  are two-hole transitions. The asymmetric broadening and the undulations of the principal bound exciton line  $A_1^y$  is due to exciton delocalization on acceptor pairs at high concentrations

<sup>3)</sup>  $\bar{N}$  increases with charge localization (see [12]).

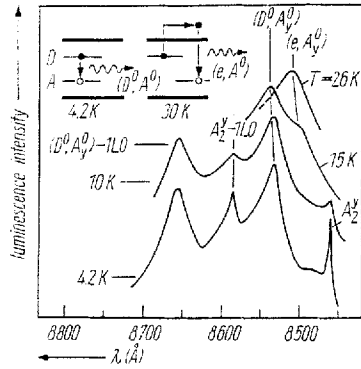


Fig. 3. Temperature dependence of the donor-acceptor pair band ( $D^0, A_Y^0$ ) and of the first two-hole transition  $A_2^Y$ . At 26 K, ( $D^0, A_Y^0$ ) is replaced by the conduction band-acceptor transition, which gives  $E_A^Y \approx 148$  meV

centers. A simple model, considering the exciton bound on an acceptor pair, fits well the observed band shape [17]. The localization energy depends on the pair separation, and for a given pair the intensity of the recombination line is proportional to the number of the available sites (for a given pair separation) in the crystal lattice. Undulations result from the statistical variations of this number.

In addition to this phenomenon, acceptors interact also with residual donors. The band ( $D^0, A_Y^0$ ) masks totally the THT lines, and is identified as the DAP band which results from the recombination of an electron bound on a donor, with a hole bound on an acceptor [7].

When  $N_A$  increases, the peak energy shifts to higher energies (Fig. 2, curves b and c). This is due to the enhanced contribution of the close pairs associated with a decrease of the mean pair distances  $R \sim N^{-1/3}$ . Indeed, the photon energy for a given pair is

$$h\nu = E_G - (E_A + E_D) + \frac{e^2}{\epsilon R} + J(R) \quad (3)$$

with  $E_A$ ,  $E_D$  the acceptor and donor binding energies,  $e$  the electronic charge,  $\epsilon$  the dielectric constant,  $J(R)$  an interaction term. ( $J(R) = 0$  when  $R \rightarrow \infty$ .)

So, when  $R$  decreases,  $h\nu$  increases.

The same shift can also be observed, when the excitation intensity increases. Since, the transition probability is proportional to the overlap of the electron and hole wave functions, so the distant pairs saturate more rapidly than the close pairs [7].

The temperature dependence of this band supports also our assignment (Fig. 3). At low temperature, we observe simultaneously ( $D^0, A_Y^0$ ) and the first THT line  $A_2^Y$ . When the temperature increases, first  $A_2^Y$  disappears rapidly as can be expected for a THT line, and secondly, ( $D^0, A_Y^0$ ) is progressively replaced by a new band at higher energy ( $e, A_Y^0$ ). This band results from the recombination of the conduction band electrons with holes bound on acceptors. The peak energy is given by [18]

$$h\nu \approx E_G - E_A + kT/2 \quad (4)$$

with  $k$  the Boltzmann constant,  $T$  the electronic temperature.

From this transition (using  $E_G = 1.606$  eV [1]), we obtain the following binding energy for the acceptor "y".  $E_A^Y \approx 148$  meV.

### 3.2 Two-hole transitions

Fig. 4 shows the detail of the THT lines for acceptor y. The pseudo-Rydberg series can be fitted by an empirical formula

$$E_n = E_0 n^{-a} \quad (5)$$

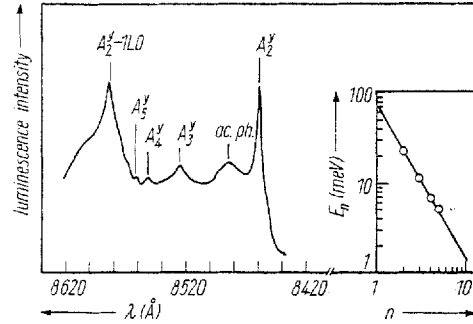


Fig. 4. Detail of the two-hole transitions for acceptor y, at 5 K. Transitions are well fitted by the quasi-hydrogenic empirical formula. The limit of this series gives  $E_A^y \approx 147$  meV.  $E_0 = 75$  meV,  $a = 1.73$ ,  $E_n = E_0 n^{-a}$

This is used because of the similarity with the hydrogen atom.  $E_0$  and  $a$  are fitting parameters. This formula has been used successfully in other materials [4, 19].

$E_n$  is the energy of the  $n$ -th excited state of the acceptor. For relatively deep acceptors (e.g. y), the central cell corrections are very important and affect the S-like states, and especially the ground state 1S. So, it is more convenient to use (5), only for the excited states, less affected by central cell corrections. The purpose of this fit being only to find the position of the line  $A_n$  when  $n \rightarrow \infty$ , (5) must be viewed only as a realistic extrapolation formula. When this limit is so estimated, the energy difference between this limit ( $n \rightarrow \infty$ ) and the PBE line  $A_1$  ( $n = 1$ ) is the acceptor binding energy  $E_A$  (i.e.  $E_{1S}$ ).

For acceptor y, the best fit is obtained for  $E_0 = 75$  meV,  $a = 1.73$ . So, we find  $E_A^y = 147$  meV (Fig. 4) in agreement with the previously obtained value.

Strong acoustic phonon replicas follow the  $A_2^y$  line. It is worth to note that the LO replica of  $A_2^y$  is slightly shifted to lower energies and deformed. This results from a resonant interaction with phonons [7, 20, 21].

### 3.3 J-J coupling

The line  $A_{11}^y$  (Fig. 1, 2) is an excited state of the PBE line  $A_1^y$ . It is known [7] that, for the neutral acceptor-bound exciton complex,  $J$ - $J$  coupling between two holes (spin 3/2) and one electron (spin 1/2), give three states 1/2, 3/2, 5/2. In final state, there is one hole.  $A_1^y$  corresponds to the transition from the 1/2 state, while  $A_{11}^y$  is associated with transitions from 3/2 and 5/2 states. When the temperature increases, we observe the thermalization between  $A_1^y$  and  $A_{11}^y$ , with an activation energy of  $\approx 1$  meV, which corresponds exactly to the energy difference between these lines.

### 3.4 Acceptor z

We have seen that the lines  $A_1^z$ ,  $A_2^z$  are related to another acceptor labeled z (Fig. 1, curve a). For long annealing times, only acceptor y can be seen. After some heat treatments, such as annealing under a flowing  $H_2$ - $N_2$  mixture, acceptor z was very strong, but, for the moment, the introduction conditions of this acceptor have not been fully established.

However, we can define some general characteristics of this acceptor. When the acceptor z series (Fig. 1, curve a) near 1.5 eV becomes more important than the acceptor y series, then, simultaneously the PBE line  $A_1^z$  dominates the PL spectrum. This is the reason that this line is attributed to the acceptor z.

The general luminescence behavior of this acceptor is exactly similar to that of acceptor y. We see the DAP transitions ( $D^0$ ,  $A_2^0$ ) near 1.491 eV. At 25 K, the conduction band-acceptor transition ( $e$ ,  $A_2^0$ ) gives approximately the binding energy  $E_A^z \approx 108$  meV.

Since the concentration of acceptor  $z$  cannot be exactly controlled, we could not find the ideal conditions to observe the pseudo-Rydberg series of THT lines. Only the first THT line  $A_2^z$  is observed at 1.5010 eV and gives 87.6 meV for the 1S-2S energy level separation.

#### 4. Li Diffusion

After Li diffusion (see Section 2), following the diffusion temperature and time, acceptor concentrations as high as  $10^{17} \text{ cm}^{-3}$  can be obtained. The diffusion of Li is well controlled, and it can be incorporated at concentrations between  $10^{15}$  and  $10^{17} \text{ cm}^{-3}$ .

For a detailed analysis of PL spectra, it is more convenient to have low doping levels in order to prevent line broadening. The best result is obtained after a diffusion at 450 °C for 20 min (Fig. 5). The key feature is the appearance of a new luminescence band near 8000 Å (Fig. 5, curve a), simultaneously with a new PBE line  $A_1^{\text{Li}}$  at 1.5894 eV, which is well distinguished from  $A_1^{\text{V}}$  (Fig. 5, curve d). For comparison, the PBE lines of the undoped sample is shown (Fig. 5, curve e). In this slightly diffused sample we have  $N_A - N_D \approx 10^{15} \text{ cm}^{-3}$ , while for higher doping levels, it is difficult to observe the splitting of the PBE line.

The luminescence band near 8000 Å has a complex structure, with sharp lines superimposed on a broad band. The peak energy of this band is at 1.540 eV (Fig. 5, curve a). Fig. 5, curve b is recorded at very low excitation level (50 μW instead of 50 mW for a spot diameter of about 0.5 mm). In this case, we reach a quasi-equilibrium situation and saturation effects disappear, and especially, the DAP band and the conduction band-acceptor transitions are well separated [22]. The band at 1.540 eV ( $D^0, A_{\text{Li}}^0$ ) is identified as DAP transition between the acceptor Li and the unidentified donor. At low excitation, it shifts to lower energy (Fig. 5, curve b). When the temperature

increases, a new band ( $e, A_{\text{Li}}^0$ ) at higher energy grows up, at the expense of ( $D^0, A_{\text{Li}}^0$ ). This is the conduction band-acceptor Li transition. In fact the spectral shape and temperature dependence can be fitted very well with a simple theoretical curve [22, 23].

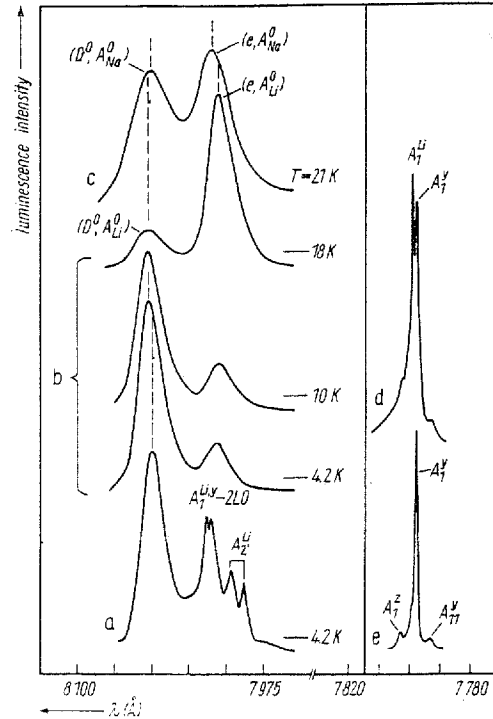


Fig. 5. Photoluminescence of slightly Li diffused CdTe with  $N_A - N_D \approx 10^{15} \text{ cm}^{-3}$  (a) at normal excitation level (50 mW laser power on 0.5 mm diameter), (b) at low excitation level, (c) Na diffused sample, (d) the new PBE line  $A_1^{\text{Li}}$  in Li diffused sample, (e) as-grown sample

From the peak energy of ( $e$ ,  $A_{Li}^0$ ) and with the formula (4) we obtain the Li acceptor binding energy  $E_A^{Li} \approx 57.8$  meV.

At low temperature and at normal excitation level (Fig. 5, curve a), we observe a doublet structure labeled  $A_2^{Li}$ . This doublet is systematically observed in any Li diffused sample. Their peak energies are at 1.5516 eV ( $A_{2a}^{Li}$ ) and 1.5499 eV ( $A_{2b}^{Li}$ ), and their relative intensities are constant (ratio  $\approx 1$ ). They are shifted by 37.8 and 39.5 meV, respectively, from the PBE line  $A_1^{Li}$ . The magnitude of these energies would correspond approximately to the energy difference  $E(1S) - E(2S)$  which can be expected for a shallow acceptor as Li [4, 24]. So, these lines are suspected of being the first THT line (to the 2s state) of the Li acceptor. They disappear rapidly when the temperature increases. Their LO phonon replicas are shifted to higher energy. Normally the LO phonon energy is 21.3 meV in CdTe, while the separation between  $A_{2a}^{Li}$ ,  $A_{2b}^{Li}$ , and their LO phonon replicas is 19.1 meV.

This phenomenon has been already observed in other materials [4, 7, 20, 21], for THT, and is well explained by interaction between a LO phonon and the bound particle. If the LO phonon energy is somewhat greater than the bound particle binding energy, the following virtual interaction can occur:

LO phonon + neutral center  $\rightleftharpoons$  ionised center + free particle

This is the reason why a distortion of the LO phonon replica can be observed for the excited states, but not for the ground state. The same shift is observed also for acceptor y (see Section 3), but the magnitude of this interaction decreases with the acceptor ionization energy [21].

However, if  $A_{2a}^{Li}$  and  $A_{2b}^{Li}$  are effectively THT lines, this doublet structure is unusual. The width of these lines ( $\approx 0.8$  meV) is also too large. As in silicon, a resonant interaction with phonons can be suspected [25]. In contrast with the interaction described above, which involves excitation to the continuum state, this latter interaction would involve excitation between discrete bound states of the bound particle. If this excitation energy (e.g.  $E(1S) - E(2S)$ ) is close to a phonon energy (e.g. 2LO, TO + LO, etc.) of the material, a resonant interaction can occur. The result is a doublet structure, a broadening, and an energy shift. In this case, the measured energy difference between  $A_1^{Li}$  and the doublet  $A_2^{Li}$  does not correspond exactly to the 1S-2S energy separation. This latter value can be estimated with the use of the formulas established for silicon [25]. Tentatively, if an interaction is considered with phonons (e.g. 2TO phonons), 1S-2S energy would be about 41 meV. This energy is close to the value obtained by resonant excitation of DAP pairs [24] or by infrared absorption [26].

### 5. Na Diffusion

Na can also be introduced in CdTe, with the same diffusion procedure as for Li. But its diffusion is not controlled as well as for Li. Especially we could not observe any THT. Systematically, donor concentrations are enhanced considerably for an unknown reason, while such an effect has never been obtained in the case of Li diffusion.

In spite of these difficulties, Na diffusion has two characteristic effects on the PL spectra. First, the donor related lines ( $D_1$ ,  $D_2$ ) become comparable to the acceptor lines. Secondly, a new PBE line  $A_1^{Na}$  at about the same energy as  $A_1^{Li}$  is obtained, and as we can see on Fig. 5c, a new conduction band-acceptor transition exists ( $e$ ,  $A_1^{Na}$ ). This transition is slightly shifted to lower energy with respect to the Li associated band.

It gives the following ionization energy for the Na acceptor:  $E_A^{Na} \approx 58.8$  meV.

## 6. Discussion

We have shown that Li and Na introduce two shallow acceptor levels. Energy levels and diffusion properties of Li in CdTe have already been published [24, 26, 27], but to our knowledge the luminescence properties of Li we have observed (THT lines with a doublet structure,  $(e, A_{Li}^0)$  transition, splitting of the PBE line ...), have never been reported before. The published energy level scheme of Li was obtained after fitting with a theoretical model, the result of donor-acceptor pair excitation spectroscopy [24].

This fit gives the value of 60.7 meV for the ionization energy, with a 2S level energy of 18.2 meV. The results obtained by infrared absorption experiments [26] are close to these, and are 61.4 and 19.7 meV for 1S (i.e.  $E_A$ ) and 2S levels, respectively.

Our results (57.8 and 16.8 meV, respectively) are in approximate agreement with these values, but essentially the ionization energy is about 3 meV smaller.

It is difficult to make a rigorous comparison between different results, since binding energies are obtained in different ways:

DAP excitation spectroscopy or the infrared absorption, require a theoretical fit to give the energy levels, while the  $(e, A_{Li}^0)$  transition gives directly the binding energy with formula (5), on condition that we know exactly the band-gap energy  $E_G$ . Nevertheless, discrepancies of  $\approx 3$  meV are difficult to be explained.

For the other acceptors y and z, we report for the first time the observation of THT lines. An acceptor near 150 meV has been reported and frequently attributed to a cadmium vacancy-donor complex [1]. In ZnTe, a similar acceptor level which was attributed to a native defect, has been recently identified as Cu in Zn site [4, 28]. In ZnTe, all the dominant acceptor levels have been demonstrated to be due to substitutional impurities [4, 5]. In Table 1, we present some of the ZnTe results, in comparison with those obtained in CdTe.

Table 1

Comparative results for shallow acceptors in ZnTe (see [3, 5, 28]) and CdTe. For Li in CdTe, values in parentheses are tentatively obtained with the hypothesis of resonant interaction with phonons (see text)

| ZnTe |                |             |                |                 | CdTe |                |             |                |                 |
|------|----------------|-------------|----------------|-----------------|------|----------------|-------------|----------------|-----------------|
|      | $E_A$<br>(meV) | 2S<br>(meV) | 1S-2S<br>(meV) | $A_1^x$<br>(eV) |      | $E_A$<br>(meV) | 2S<br>(meV) | 1S-2S<br>(meV) | $A_1^x$<br>(eV) |
| Li   | 60.5           | 17.1        | 43.4           | 2.3746          | Li   | 57.8           | (16.8)      | (41)           | 1.5894          |
| Na   | 62.8           | 18.2        | 44.6           | 2.3743          | Na   | 58.8           | —           | —              | 1.5893          |
| k    | 113            | 20.2        | 92.8           | 2.3736          | z    | 108            | 20.4        | 87.6           | 1.5886          |
| Ag   | 121            | 20.7        | 100.3          | 2.3736          |      |                |             |                |                 |
| Cu   | 149            | 23.9        | 125.1          | 2.3746          | y    | 147            | 22.6        | 124.4          | 1.5896          |

Li, Na energies are comparable. For y, there is a great similarity with Cu in ZnTe. Their luminescence properties as well as their enhancement on annealing of the sample, are identical. So, we believe that y is due to Cu in Cd site.

For the acceptor z, the similarity is with the unknown k acceptor of ZnTe, as well as with Ag.

In Table 1, the position of the PBE line  $A_1^x$  for each acceptor is also indicated. A comparison with ZnTe, where these lines are identified without any doubt, support

our assignments, since the relative energy positions are identical. We remark that Haynes' rule [29] is disobeyed as in ZnTe.

Further backdoping experiments are presently in progress in order to identify definitely the levels associated with Cu and Ag.

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